CBSE Test Paper - 01

Class - 12 Chemistry (Amines)

1. In a reaction, a secondary amine forms Nitrosoamine (R_2N-N=O), which on heating with phenol and conc H_2SO_4 gives a green colour solution which turns blue on adding alkali. The reaction is called:
   a. Fries reaction
   b. Perkin's reaction
   c. Libermann's nitroso reaction
   d. Etard's reaction
2. If the starting amide has got four carbon atoms and the amine that is formed has got only 3 carbon atoms, then the reaction is called
   a. Gabriel synthesis
   b. carbylamines reaction
   c. Hoffmann bromamide reaction
   d. Clemmensen reduction
3. When one of the following reacts with NaOH, the product is sodium benzoate?
   a. benzene hydroxide
   b. benzoic acid
   c. benzaldehyde
   d. benzene
4. The nitrogen's lone pair in pyrrolidine is best described as occupying what type of orbital?
   a. s
   b. sp^2
   c. sp^3
   d. sp
5. Which of the following reacts with $NaNO_2$ + HCI to give alcohol?
   a. $C_6H_5CH_2NHCH_3$
   b. CH_3NH_2
   c. $C_6H_5NH_2$

d. $(CH_3)_3N$

6. Write IUPAC name of the following compound and classify it into primary secondary and tertiary amine.
   $CH_3(CH_2)_2NH_2$

7. Write the reaction taking place when aniline reacts with bromine water.

8. How is orange I prepared?

9. It is difficult to prepare pure amines by ammonolysis of alkyl halides. Give reasons.

10. Why are amines more basic than the comparable alcohols.

11. Write the chemical equations to illustrate the following reactions:
    i. Sandmeyer reaction.
    ii. Coupling reaction.

12. Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reaction involved.

13. Identify the compounds A, B, C in the following equation.
    $$C_6H_5CONH_2 \xrightarrow[SOCl_2]{P_2O_5\ or} (A) \xrightarrow{catalytic\ reduction} (B) \xrightarrow[NaNO_2/HCl]{HONO\ or} (C)$$

14. Write an equation of the reaction of aniline with benzoyl chloride and write the name of the product obtained.

15. Write short notes on the following:
    i. Carbylamine reaction
    ii. Diazotisation
    iii. Hofmann's bromamide reaction
    iv. Coupling reaction
    v. Ammonolysis

CBSE Test Paper - 01

Class - 12 Chemistry (Amines)

Solutions

1. (c) Libermann's nitroso reaction

   Explanation: This is Libermann's nitroso reaction. Secondary amines react with HNO_2 to give N-N nitrosodialkylamine (R_2N-N=O). Nitrosamines are water-soluble yellow oils which when warmed with phenol and conc. H_2SO_4 give green color solution and with alkali, they give a blue color solution. Tertiary amines do not react with nitrous acid.
2. (c) Hoffmann bromamide reaction

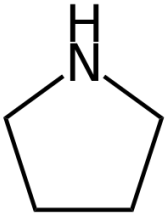
   Explanation: In Hoffmann bromamide degradation reaction, the amine formed has one carbon less than the amide.

   $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
3. (b) benzoic acid

   Explanation: Benzoic acid reacts with NaOH to form sodium benzoate, this is a neutralisation reaction where acid reacts with a base to give salt and water.

   $C_6H_5COOH + NaOH \rightarrow C_6H_5COO^-Na^+ + H_2O$
4. (c) sp^3

   Explanation: Pyrrolidine is tetrahydropyrrole.

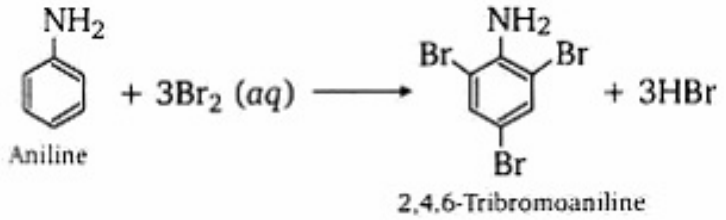
   

   The nitrogen atom in pyrollidine is sp^3 hybridized. Two sp^3 hybridized orbitals are involved in pairing with carbon, one sp^3 hybridized orbital is involved in pairing with hydrogen and one sp^3 hybridized orbital is occupied by a lone pair.
5. (b) CH_3NH_2

   Explanation: Aliphatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and a mineral acid such as HCl) to form aliphatic diazonium salts, which

is unstable and decomposes to give a carbocation and evolve N_2 gas. The carbocation so formed reacts with water from medium to give further produce alcohol.

6. Propane-1-amine (1°),

7. 

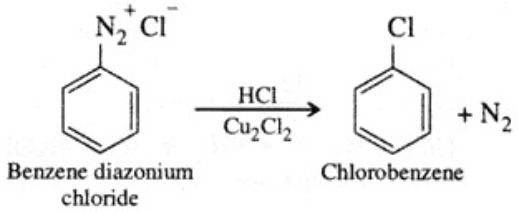
8. It is obtained by coupling reaction between diazotized sulphanilic acid and alkaline solution of β Napthol.

9. The process of ammonolysis yields a mixture of primary, secondary, tertiary amines and quaternary salts. This is because the primary amine formed can further react with the alkyl halide to form the secondary amine, which in turn will again react with the alkyl halide to form the tertiary amine, which also reacts with the alkyl halide leading to the formation of quaternary salt. Thus such a reaction would form a mixture of all the four compounds and it will be difficult to get the pure amine.

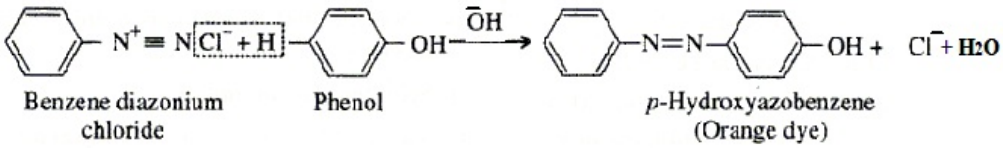
$$Rx \xrightarrow[-Hx]{NH_3} RNH_2 \xrightarrow[-Hx]{Rx} R_2NH \xrightarrow[-Hx]{Rx} R_3N \xrightarrow{Rx} [R_3N]^+X^\bullet$$

10. Amines are more basic than alcohols because lone pair in nitrogen is more available for incoming accepter as compared to oxygen as oxygen is more electronegative than nitrogen.

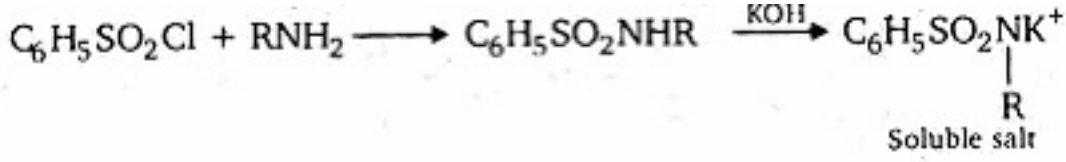
11. i. Sandmeyer reaction:



ii. Coupling reaction:

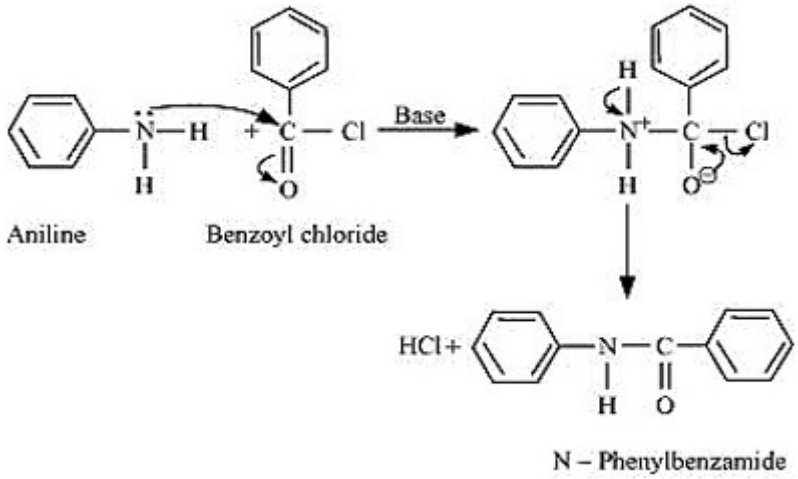


12. Primary, secondary and tertiary amines can be identified by Hinsberg's reagent (Benzenesulphonyl chloride $C_6H_5SO_2Cl$). Primary amines react with Hinsberg's reagent to form sulphonamides soluble in alkali whereas secondary amines form sulphonamides insoluble in alkali. Tertiary amines do not react with Hinsberg's reagent.



$$C_6H_5SO_2Cl + R_2NH \rightarrow C_6H_5SO_2NR_2 \xrightarrow{KOH} \text{Insoluble}$$

13. $C_6H_5CONH_2 \xrightarrow[SOCl_2]{P_2O_5\ or} \underset{(A)}{C_6H_5CN} \xrightarrow{catalytic\ reduction} \underset{(B)}{C_6H_5CH_2NH_2} \xrightarrow[NaNO_2/HCl]{HONO\ or} \underset{(C)}{C_6H_5CH_2OH}$

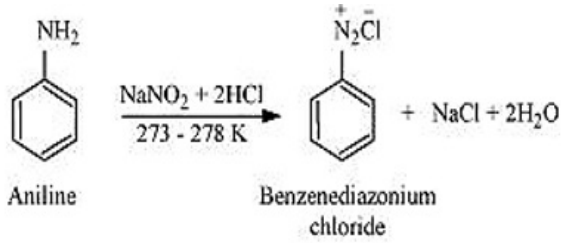
14. 

15. i. **Carbylamine reaction:** Carbylamine reaction is used as a test for the identification of primary amines. When aliphatic and aromatic primary amines are heated with chloroform and ethanolic potassium hydroxide, carbylamines (or isocyanides) are formed. These carbylamines have very unpleasant odours. Secondary and tertiary amines do not respond to this test. For example,

$$\underset{Methana\,mine}{CH_3-NH_2} + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{Methyl\ carbylamine}{CH_3-NC} + 3KCl + 3H_2O$$

ii. **Diazotisation:** Aromatic primary amines react with nitrous acid (prepared in situ from $NaNO_2$ and HCl) at 273 - 278 K to form diazonium salts. This conversion

of aromatic primary amines into diazonium salts is known as diazotization. For example,

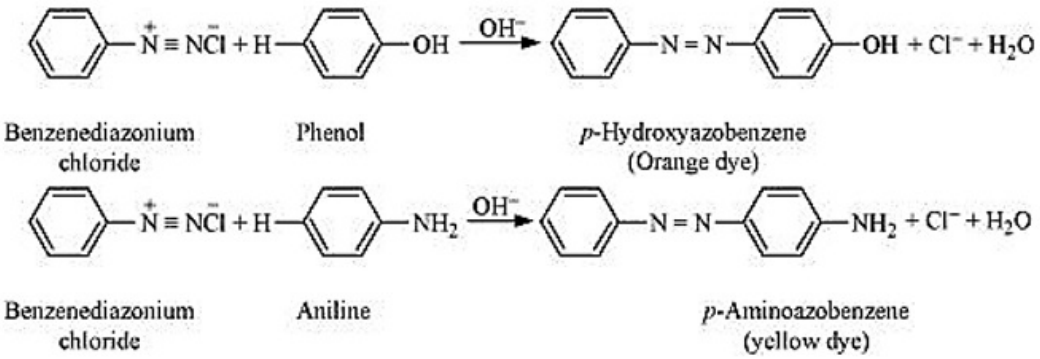


iii. **Hoffmann bromamide reaction:** When an amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide, a primary amine with one carbon atom less than the original amide is produced. This degradation reaction is known as Hoffmann bromamide reaction. This reaction involves the migration of an alkyl or aryl group from the carbonyl carbon atom of the amide to the nitrogen atom. For example,

$$\underset{Ethanamide}{CH_3-\overset{O}{\overset{||}{C}}-NH_2} + Br_2 + 4NaOH \rightarrow \underset{Methanamine}{CH_3-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

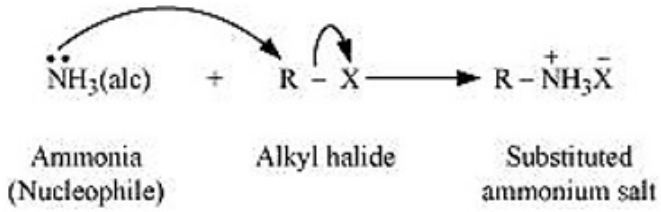
$$\underset{Benzamide}{C_6H_5-\overset{O}{\overset{||}{C}}-NH_2} + Br_2 + 4NaOH \rightarrow \underset{Aniline}{C_6H_5-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

iv. **Coupling reaction:** The reaction of joining two aromatic rings through the - N = N - bond is known as coupling reaction. Benzene diazonium salt reacts with phenol or aromatic amines to form coloured azo compounds.



v. **Ammonolysis:** When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino $(-NH_2)$ (-NH_2) group. This

process of cleavage of the carbon-halogen bond is known as ammonolysis.



When this substituted ammonium salt is treated with a strong base such as sodium hydroxide, amine is obtained.

$$R-\overset{+}{N}H_3\overset{-}{X}\ +\ NaOH \rightarrow \underset{Amine}{R-NH_2} +\ H_2O\ +\ NaX$$

Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt as shown.

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{Quaternary\ ammonium\ salt}{R_4\overset{+}{N}\overset{-}{X}}$$

CBSE Test Paper - 02

Class - 12 Chemistry (Amines)

1. Direct nitration of aniline yields significant amount of meta derivative. To obtain more p – nitro derivative, one or more of the below can be done
   a. All of these
   b. by increasing temperature
   c. controlling the nitration reaction
   d. reacting with acetic anhydride
2. The following amine can be classified as $(C_2H_5)_2CHNH_2$
   a. Tertiary
   b. Secondary
   c. Mixed
   d. Primary
3. Heating a(n) ____ results in a Cope elimination.
   a. imine
   b. amine oxide
   c. enamine
   d. oxime
4. Which of the following is an intermediate in the mechanism for amide synthesis through acylation?
   a. A
   b. B
   c. C
   d. D
5. Amide which gives propanamine by Hoffmann bromamide is:
   a. Pentanamide
   b. Hexanamide
   c. Butanamine
   d. Propanamine

6. Why does acetylation of $-NH_2$ group of aniline reduce its activating effect?

7. Mention one commercial use of N, N-Dimethyl aniline (DMA).

8. Write IUPAC name of the following compound and classify it into primary secondary and tertiary amine.
   $(CH_3CH_2)_2NCH_3$

9. Accomplish the following conversion: Nitrobenzene to benzoic acid.

10. Give a chemical test to distinguish between aniline and ethylamine.

11. Give one example of Hoffmann - bromamide degradation reaction.

12. A compound X having a molecular formula, C_3H_7NO reacts with Br_2 in presence of KOH to give another compound Y. The compound Y reacts with HNO_2 to form ethanol and N_2 gas. Identify the compounds X and Y and write the reactions involved.

13. Arrange the following in increasing order of their basic strength:
    i. $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5\ CH_2NH_2$ and $(C_2H_5)_2NH$
    ii. $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and $C_6H_5NH_2$
    iii. $CH3NH_2$, $(CH_3)_2NH$, $(CH3)_3N$, $C_6H_5NH_2$ and $C_6H_5CH_2NH_2$

14. Give reasons:
    Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide.

15. Accomplish the following conversion: Aniline to benzyl alcohol.

CBSE Test Paper - 02

Class - 12 Chemistry (Amines)

Solutions

1. (d) reacting with acetic anhydride

   Explanation: Direct nitration of aniline yield significant amount of meta derivative, this is because the use of HNO_3 during nitration of aniline causes the formation of anilinium ion($C_6H_5NH_3^+$). Anilinium ion is responsible for the formation of metra nitro aniline. To prevent this, initial reaction of aniline with acetic anhydride acetylates -NH_2 group.

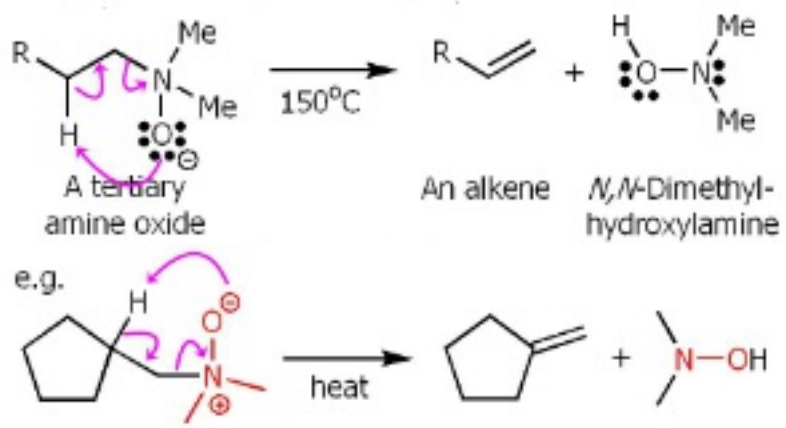
   $C_6H_5NH_2$ + $CH_3COOCOCH_3$ → $C_6H_5NHCOCH_3$.

   Now, -$NHCOCH_3$ is an activating group, which on nitration followed by hydrolysis form para nitro aniline as a major product.
2. (d) Primary

   Explanation: This is primary amine, because the Nitrogen of amine is only connected to one carbon.
3. (b) amine oxide

   Explanation: Heating of Amine oxide result in cope elimination which is cis/syn elimination.

   The Cope reaction or Cope elimination, is an elimination reaction of the N-oxide of a tertiary amine to form an alkene and a hydroxylamine.



4. (a) A

   Explanation: A is the intermediate formed by nucleophilic attack by CH_3NH_2 on the

carbonyl carbon of CH_3COCl.

5. (c) Butanamine

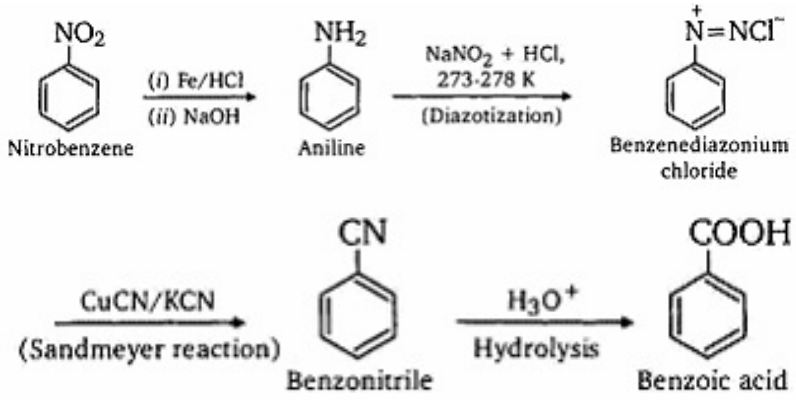
   Explanation: In Hoffmann bromamide reaction, the amine formed has one carbon less than the amide.

   $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

6. Due to resonance the lone pair of nitrogen is less available for donation.

7. It is used as raw materials in the preparation of a number of dyes for example: methyl orange, crystal violet, malachite green etc.

8. N-Ethyl-N-methylhexanamine (3°),

9. 

10. Aniline will give the azo dye test while ethylamine will not give. In azo dye test aromatic primary amines react with $NaNO_2$ and HCl at 273-278 K to form diazonium salts which on further reaction with alkaline solution of β -naphthol give orange red dye.

11. In Hoffmann – bromamide reaction an acid amide is reacted with bromine in presence of the aqueous or ethanolic solution of NaOH to give a primary amine having one carbon less than that present in amide.

    $CH_3CONH_2 + Br_2 + 4\ NaOH \rightarrow CH_3NH_2 + Na_2CO_3 + 2\ NaBr + 2\ H_2O$

12. $\underset{\substack{\text{'X' Propanamide} \\ (\text{Mol Formula} = C_3H_7NO)}}{CH_3CH_2CONH_2} + Br_2 + 4KOH \rightarrow \underset{\text{'Y' Ethanamine}}{CH_3CH_2NH_2} + HNO_2 \rightarrow CH_3CH_2OH + N_2 +$

H_2O

13. i. $C_6H_5NH_2 < C_6H_5CH_2NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

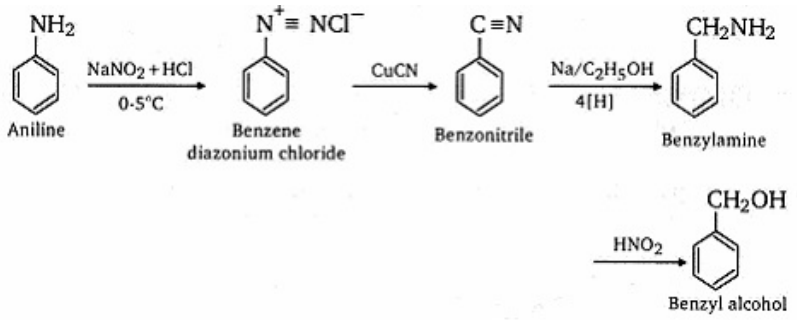
    ii. $C_6H_5NH_2 < C_2H_5NH_2 < (C2H_5)_3N < (C_2H_5)_2NH$

    iii. $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

14. Methylamine being basic, accepts a proton from water as shown in the equation below. While doing so it liberates a OH^- ion which combines with $FeCl_3$ to form a brown ppt of ferric hydroxide.

$$CH_3NH_2 + H_2O \rightarrow CH_3\overset{+}{N}H_3 + OH^-$$

$$FeCl_3 + 3OH^- \rightarrow \underset{(reddish\ brown\ ppt.)}{Fe(OH)_3} + 3Cl^-$$

15. 

CBSE Test Paper - 03

Class - 12 Chemistry (Amines)

1. The following compound is called

   a. None of the below
   b. 4 – aminocyclohexane
   c. pyrrole
   d. 4 – aminocyclohexanene
2. The molecular formula of ethyl acetate is
   a. C_4H_8O
   b. $C_4H_8O_2$
   c. $C_5H_{10}O_2$
   d. $C_5H_8O_2$
3. The nitrogen atom of trimethylamine is _____ hybridized which is reflected in the CNC bond angle of _____.
   a. sp^3,120°
   b. sp^2, 120°
   c. sp^3, 108°
   d. sp^2, 108°
4. Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole

   a. ortho and para in equal amounts
   b. major product is ortho nitroanisole

c. None of these
d. major product is para nitroanisole

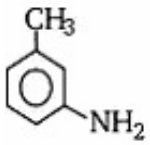
5. Which one of the following cannot be obtained by Gabriel phthalimide synthesis?
   a. CH_3NH_2
   b. None of these
   c. $CH_3CH_2NH_2$
   d. Aromatic primary amines

6. Write the chemical equation for the following chemical reaction: A primary amine is prepared from a primary alkyl halide.

7. Give IUPAC name of sulphanilic acid.

8. What is Heinsberg reagent?

9. Identify A and B in the following reactions:
   $CH_3COOC_2H_5 \xrightarrow{NH_3} A \xrightarrow{Br_2/KOH} B$

10. Write the common and IUPAC names of the following compound;
    

11. Before reacting aniline with for HNO_3 nitration, it is converted to acetanilide. Why is this done and how is nitroaniline obtained subsequently?

12. An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N C_6H_7N.Write the structures and IUPAC names of compounds A, B and C.

13. Mention two important uses of sulphanilic acid.

14. Arrange the following in increasing order of their basic strength in aqueous solution:
    1. $C_2H_5NH_2, C_6H_5NH_2, NH_3, C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
    2. $C_2H_5NH_2, (C_2H_5)_2NH, (C_2H_5)_3N, C_6H_5NH_2$

3. $CH_3NH_2, (CH_3)_2NH, (CH_3)_3N, C_6H_5NH_2, C_6H_5CH_2NH_2$

15. i. How will you convert:
    a. Nitrobenzene to phenol,
    b. Aniline to chlorobenzene

    ii. Identify the compounds A, B and C in the following reactions:

    a. $A \xrightarrow[NaOH]{Br_2} B \xrightarrow{HNO_2} C \xrightarrow[I_2]{\text{Red } P} CH_3$

    b. $A \xrightarrow{dil.\ HNO_3} B \xrightarrow{Sn/HCl} C \xrightarrow[Boil]{NaNO_2+HCl}$ 

    c. $A \xrightarrow{\Delta} B \xrightarrow[KOH]{Br_2} C \xrightarrow{HNO_2} C_2H_5OH$

CBSE Test Paper - 03

Class - 12 Chemistry (Amines)

Solutions

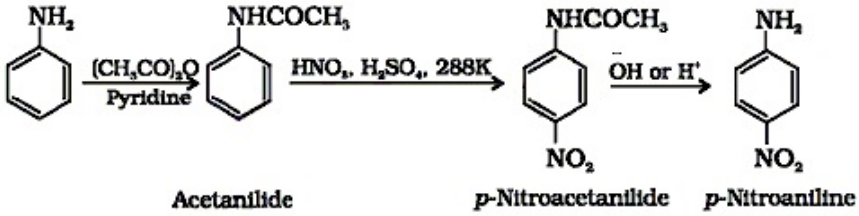
1. (c) pyrrole
   Explanation: This is pyrrole, a heterocyclic compound.
2. (b) $C_4H_8O_2$
   Explanation: Its molecular formula is $C_4H_8O_2$ and its chemical formula is $CH_3COOC_2H_5$.
3. (c) sp^3, 108°
   Explanation: The N atom uses its one 2s and three 2p orbitals for sp^3 hybridisation and the bond angle is 108° less than normal tetrahedral bond angle due to lone pair-bond-pair repulsion which is more than bondpair - bond pair repulsion.
4. (d) major product is para nitroanisole
   Explanation: In p-nitroanisole, the lone pair on oxygen is in conjugation with the pi bond of the benzene ring. Due to resonance, the nucleophilic centers are created at ortho and para positions. -OCH_3 hence is an activating group and hence o/p activating. The NO_2^+ ion can attack at ortho and para positions, but since steric hindrance is least at para position, the major product is p-nitroanisole.
5. (d) Aromatic primary amines
   Explanation: In Gabriel phthalimide reaction, a potassium salt of phthalimide is formed. It reacts readily with the primary alkyl halide to form the corresponding alkyl derivative. But aryl halide (C_6H_5X) does not react with potassium salt of phthalimide. Because C-X bond in haloarene (alkyl halide) is difficult to be cleaved due to a partial double bond character and hence, do not undergo SN_2 reaction with potassium salt of phthalimide. So, aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
6. $RX + NH_3 \rightarrow RNH_2 + HX$
7. 4-Aminobenzene sulphonic acid.

8. Hinsberg reagent is benzenesulphonyl chloride $(C_6H_5SO_2Cl)$

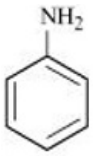
9. $\underset{Ethyl\ ethanoate}{CH_3COC_2H_5} \xrightarrow{NH_3} \underset{Ethanamide}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{Methanamine}{CH_3NH_2}$

10. The IUPAC name of the compound is 3-Methylaniline and the common name is m-Toluidine.

11. On direct nitration, aniline gets oxidized and protonated and besides ortho and para derivatives, 47% m-nitroaniline is also formed. Therefore, it is converted into acetanilide and then nitrated to give p-nitro derivative as major product.

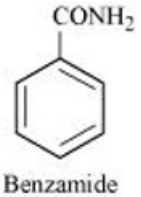


12. It is given that compound 'C' having the molecular formula, C_6H_7N and formed by the reaction of compound 'B' with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound 'B' is an amide and compound 'C' is an amine. The only amine having the molecular formula C_6H_7N is aniline, $(C_6H_5NH_2)$



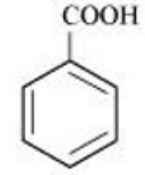
Aniline

Compound 'B' (from which 'C' is formed) must be benzamide, $(C_6H_5CONH_2)$



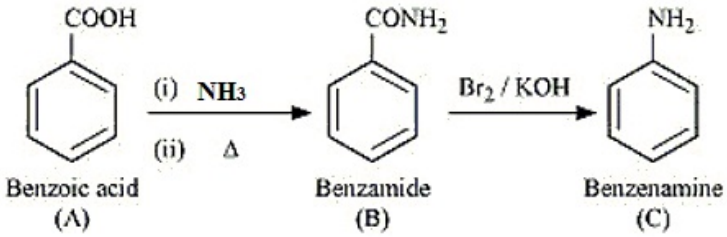
Benzamide

Further, benzamide is formed by heating compound 'A' with aqueous ammonia. Therefore, compound 'A' must be benzoic acid.

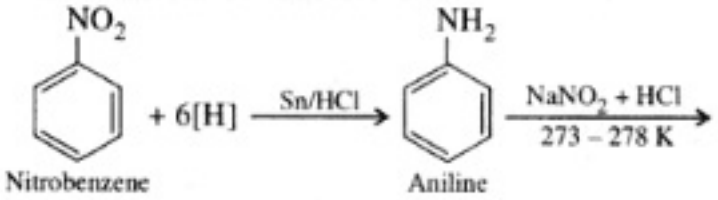


Benzoic acid

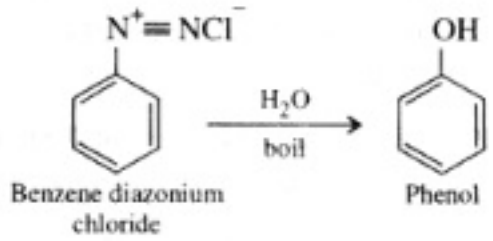
The given reactions can be explained with the help of the following equations:



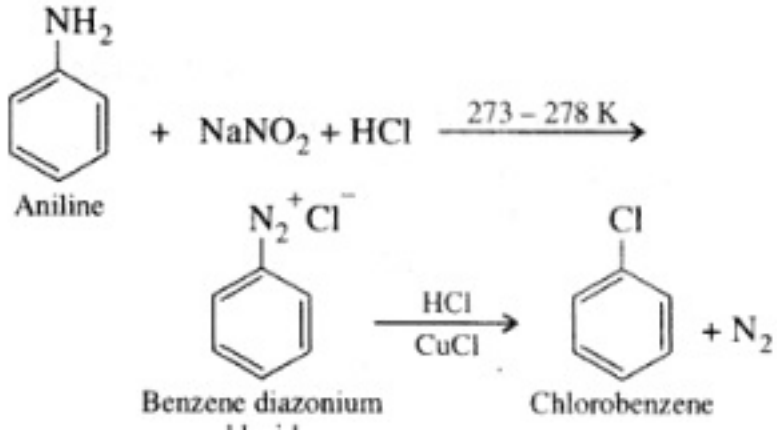
13. Salphanilic acid is used in the manufacture of:
    i. Dyes
    ii. Sulpha drugs.
14. i. $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$
    ii. $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$
    iii. $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$
15. i. Steps involved in the conversions are given below:



a.



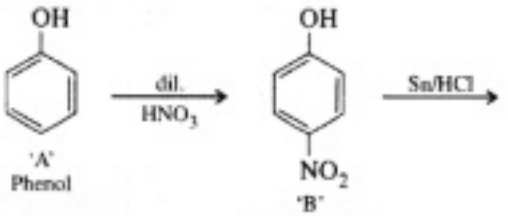
b.

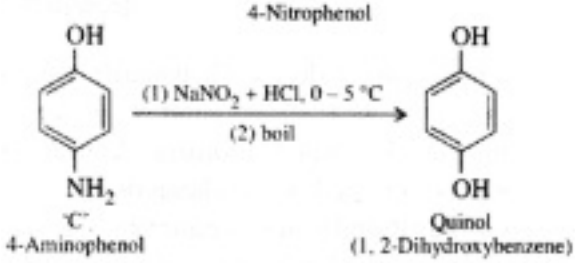


ii. A, B and C are identified as under:

a. $\underset{\substack{'A'\\Ethanamide}}{CH_3CONH_2} \xrightarrow[NaOH]{Br_2} \underset{\substack{'B'\\Methanamine}}{CH_3NH_2} \xrightarrow{HNO_2} \underset{\substack{'C'\\Methaonol}}{CH_3OH} \xrightarrow{P/I_2} \underset{Iodomethane}{CH_3I}$

b.





c. $\underset{'A'}{CH_3CH_2COONH_4} \xrightarrow{Heat} \underset{'B'}{CH_3CH_2CONH_2}$

A min *ophenol* — Pr *opana* mi *de*

$\xrightarrow[KOH]{Br_2} \underset{'C'}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{Ethanol}{CH_3CH_2OH}$

Pr *opana* min *e*